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DIFFUSION IN SILICATE MELTS

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## INTRODUCTION

Many well-known features of igneous rocks are clearly the result of diffusion. The growth of crystals is accomplished largely by the diffusion of material to crystalline nuclei. Inclusions often exhibit solution at their borders and some diffusion of their material into the surrounding magma. These phenomena involve diffusion through short distances and there is no theoretical objection to the acceptance of diffusion at the required rate. At the same time it has often been inferred that large quantities of matter have diffused through considerable distances. This has been done for the purpose of explaining various associations of igneous rocks and especially the formation of basic border phases. Since Becker's destructive criticism of this view<sup>1</sup> many geologists, but not all, have been less willing to assign to diffusion any important rôle in the production of such features.

Becker's objection was based on the extreme slowness of diffusion in all cases where its rate had been determined. The principal data then available referred to the diffusion of salts in aqueous solution, and it was on the basis of reasonable deduction

<sup>1</sup> *American Journal of Science* (4) Vol. III (1897), p. 27.

from these data that Becker's objection was raised. There has been as yet no discovery of a general principle connecting the rate of diffusion of matter in solution with other physical constants. Each substance has its coefficient of diffusivity (in a given medium) characteristic of the substance and determinable only by experiment. The coefficient is the constant factor,  $k$ , in the equation expressing Fick's law of the rate of diffusion, viz.,

$$\frac{dc}{dt} = k \cdot \frac{d^2c}{dx^2},$$

and is evidently equal to the number of grams which diffuse past 1 square centimeter of any plane in unit time when the concentration gradient normal to the plane is unity. This is a very small quantity for substances investigated. For most salts in aqueous solution it is of the order  $3 \times 10^{-6}$  in cm.<sup>2</sup> per second at the ordinary temperature and increases rapidly with rise of temperature; for molten metals it is considerably larger and of the order  $3 \times 10^{-5}$ , again increasing with rise of temperature.<sup>1</sup>

In the case of the quite different type of matter, molten silicates, it is perhaps not probable, but nevertheless not inconceivable, that the coefficient of diffusivity should be fairly large at the high temperatures concerned in spite of the usual high viscosity. Only actual measurements can make us at all certain that we have a firm basis of fact for the discussion of diffusion in molten silicates. Practically no measurements have been made. Endell has demonstrated the fact of the interdiffusion of lime and microcline glass.<sup>2</sup> Schulze has measured the rate of migration of silver ion in glass.<sup>3</sup> Indeed, it is perhaps principally from the problems of glass manufacture that we gain our impressions of diffusion in molten silicates. There diffusion is often excessively slow, but it should be noted that glasses belong for the most part among the very viscous silicate mixtures. On account of the lack of experimental data it was considered advisable to undertake some measurements of the

<sup>1</sup> Roberts-Austin found for the coefficient of diffusivity of gold into molten lead  $k = 3.47 \times 10^{-5}$  at 492°. *Roy. Soc. London, Phil. Trans.*, Vol. 187A (1896), p. 383. See also Van Orstrand and Dewey, *U.S. Geol. Survey, Prof. Paper 95-G*. 1915.

<sup>2</sup> K. Endell, *Silikat-Zeitschrift*, Vol. I, p. 195.

<sup>3</sup> *Ann. phys.*, Vol. XL (1913), p. 335.

rate of diffusion in fused rock-forming silicates. Those here described are to be considered of a preliminary nature. They are not devised with the purpose of establishing precise values for diffusion coefficients from which general theoretical conclusions might be drawn, though this is recognized as a desirable ultimate goal. They may serve rather to aid the geologist in deciding what he may and what he may not reasonably attribute to diffusion.

#### THE METHOD OF EXPERIMENT

The method followed was that of permitting the diffusion against gravity of a heavy liquid placed in the lower part of a crucible into a lighter liquid in the upper part. Ostwald has said that to make accurate experiments on diffusion is one of the hardest problems in practical physics on account of the difficulty experienced in eliminating convection currents. It is to be noted that this is especially true of aqueous solutions. Water is a thin liquid with a relatively high coefficient of thermal expansion. The driving force of convection, viz., difference of density, is therefore large and the resistance to it (viscosity) small. In silicates, however, these conditions are reversed, the viscosity being relatively great and the thermal expansion relatively small. While a small difference of temperature may establish convection in aqueous solutions, it is not to be expected to have a comparable effect in silicates. In the case of aqueous solutions the density gradient resulting from the composition gradient may be very small, but in the case of the silicates used it is quite large. If the relative densities of diopside and plagioclase liquids at high temperatures are comparable with those at lower temperatures, it can readily be shown that it would be necessary to have a temperature gradient of  $20^{\circ}$  per mm. in order to counteract the density gradient due to 1 per cent per mm. change of composition. Gradients of composition of this magnitude exist throughout most of the period of experiment. Such temperature gradients are, however, entirely lacking; not only this, but it is easy to make the moderate temperature gradient that does exist of such a sign that it acts together with the composition gradient instead of counteracting it. This is accomplished, of course, by making the temperature of the upper

part of the column higher than that of the lower part. With this end in view the crucible was suspended in most cases in a part of the furnace where the temperature increased upward. In one experiment recorded here this method of eliminating convection was replaced by a method involving the use of a bath of molten gold to obtain a uniform temperature. The platinum crucible containing the charge was protected from the molten gold by a tube of silica glass.<sup>1</sup> The silica glass was rather soft at the temperature of the experiments and required reinforcement by a tube of Marquardt porcelain. The one result obtained by this method showed no significant difference from a result obtained by the method of suspending the bare crucible in the furnace. There seemed, therefore, to be no reason for preferring the use of the gold bath and it was not carried farther.

To make assurance doubly sure in the way of minimizing possible convection, the charge was made small. This acts in three ways: to make a possible lateral difference of temperature small, to render difficult the initiation of convection currents, and to decrease the velocity of possible currents. The crucibles used were, therefore, 5 to 6 mm. in diameter and 10 to 20 mm. deep. In order to simplify the conditions of diffusion the crucibles were right circular cylinders without flare or rounded bottoms.

The temperature was kept constant partly by continual watching and regulation and partly by using current from a storage battery. In some cases an automatic regulator was used, designed by W. P. White of this Laboratory.

In each case the heavy material taken was diopside. It was first melted and then chilled to a firm cake of glass ( $G_{\frac{20}{4}} = 2.854$ ) in the bottom of the crucible. The lighter material put in the top was one of the plagioclases  $Ab_2An_1$ ,  $Ab_1, An_1$ , or  $Ab_1An_2$  ( $G_{\frac{20}{4}} = 2.483, 2.533, 2.591$  respectively). The temperature was in all cases about  $1500^\circ$ , that is, it was above the melting temperature of both layers, so that the experiments deal with diffusion of one liquid silicate into another.

<sup>1</sup> The use of silica glass in this manner was suggested by J. C. Hostetter, formerly of this Laboratory, who also kindly worked the glass into the desired form.

The charge was raised quickly to the desired temperature by plunging it into a furnace already somewhat above that temperature. After holding it for the desired length of time the charge was rapidly cooled by removal from the furnace, and the composition of the glass at various levels in the crucible was determined by measuring its refractive index, the relation between composition and refractive index having been previously determined on mixtures of known composition.

It may appear that the drastic temperature differences that arise when the cold crucible is placed in the hot furnace would be bound to set up violent convection, but fortunately this is a matter that can easily be ascertained by running a blank test. For this purpose a charge was prepared in the ordinary manner and allowed to remain in the furnace only a few minutes, when it was removed and the distribution of composition determined. It was found that the distribution was as it should be after diffusion for a short period with no random variations such as would result from convection.

In earlier experiments an ordinary thick-walled platinum crucible was used and the charge was always badly shattered in cooling. When not too numerous, the fragments were fitted together to reconstruct the original charge and the composition determined at various levels by removing a little powder with a file and determining its refractive index by the immersion method. The error involved in the measurement of the distance from the top or the bottom of the charge was large, and the results were only rough approximations. In later experiments the crucible was made of platinum foil 0.03 mm. thick. On contracting, the glass pulls the weak walls of the crucible with it and remains unshattered. The platinum foil was then peeled off and the cylinder of glass was ground to a wedge whose edge was parallel to the axis of the cylinder. The faces of the wedge were polished and the refractive index of the glass at various points was determined on the goniometer by the method of minimum deviation. The exact distance of the points from the bottom of the cylinder was measured by means of the scale on the centering screws of the goniometer.

Though numerous measurements were made by the early, rougher method, only the few made by the later method will be described. It may be noted, however, that the earlier results, within their rather large limits of error, agree with the later.

In order to obtain a visual impression of the diffusion of material, such as is obtained when copper sulphate crystals are placed in the bottom of a vessel of water, the layer of diopside was in some cases colored by the addition of 1 per cent  $\text{Fe}_2\text{O}_3$  which imparts to the glass a marked green color. In all cases the change of color was sensibly coincident with the change of refractive index; in a layer where the index fell rapidly the color faded rapidly; in cases where an upper layer was found unaffected in refraction it was likewise uncolored.<sup>1</sup>

In summary it may be stated that the mode of procedure was as follows: A layer of diopside was placed in the bottom of a crucible with a layer of plagioclase above it, diffusion was permitted at constant temperature (above the melting-temperature of both layers) for a definite period, the charge was quenched, and the composition determined at various depths by measuring the refractive index of the glass.

#### GRAPHICAL PRESENTATION OF RESULTS

The results (Table I) may be presented graphically as in

TABLE I

##### DIFFUSION RESULTS

##### EXPERIMENT NO. 24

Depth of diopside layer 1.8 mm. Total depth 9.5 mm. Time 48 hrs.										
Distance from bottom										
(mm.)	0.3	1.3	2.3	3.3	4.3	5.3	6.3	7.3	8.3	9.3
Vol. per cent diopside.	39.5	39.6	38.1	31.5	18.0	7.5	4.8	3.5	1.1	0
Plagioclase of upper layer $\text{Ab}_2\text{An}_1$ .										

##### EXPERIMENT NO. 27

Depth of diopside layer 3.2 mm. Total depth 11.7 mm. Time 48 hrs.										
Distance from bottom										
(mm.)	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Vol. per cent diopside.	52.0	51.6	50.7	49.6	46.5	33.7	9.7	2.4	0.7	0
Plagioclase of upper layer $\text{Ab}_2\text{An}_1$ .										

<sup>1</sup> This result might be taken as indicating that selective diffusion was unimportant, though not necessarily absolutely lacking.

## EXPERIMENT NO. 21

Depth of diopside layer 3.9 mm. Total depth 9.1 mm. Time 22 hrs.  
 Distance from bottom  
 (mm.)..... 0.2 1.0 2.0 4.0 5.0 6.0 7.0 8.0 8.8  
 Vol. per cent diopside.. 48.0 47.9 47.5 45.5 43.0 41.0 36.5 30.5 29.5  
 Plagioclase of upper layer  $Ab_7An_3$ .  
 Immersed in bath of molten gold.

## EXPERIMENT NO. 37

Depth of diopside layer 7 mm. Total depth 10.2 mm. Time 17 hrs.  
 Distance from bottom  
 (mm.)..... 0.3 1.3 3.3 4.3 5.3 6.3 7.3 8.3 9.3 9.5  
 Vol. per cent diopside. 73.0 72.8 72.3 70.5 70.7 68.5 66.5 64.2 63.6 63.4  
 Plagioclase of upper layer  $Ab_7An_3$ .

## EXPERIMENT NO. 25

Depth of diopside layer 3.2 mm. Total depth 14.5 mm. Time 22.5 hrs.  
 Distance from bottom  
 (mm.). 1.3 2.3 3.3 4.3 5.3 6.3 7.3 8.3 9.3 10.3 11.3 12.3 13.3 14.2  
 Vol. per cent diop-  
 side...42.5 38.3 36.3 29.8 24.4 21.3 20.1 17.8 17.2 15.0 14.6 9.5 9.0 7.3  
 Plagioclase of upper layer  $Ab_7An_3$ .

Figures 1-5, in which the ordinates represent height in millimeters above the bottom and the abscissae composition in units per cent of diopside. The initial condition will then be represented by two vertical lines indicating two uniform layers, one at 100 per cent diopside and of a length corresponding to the depth of the diopside layer, the other at 0 per cent diopside representing the layer of plagioclase above it and of appropriate length. These are joined by a horizontal line indicating instantaneous change of composition. The final condition will be represented by a curve on which any point represents the composition at the corresponding level. The slope at any point indicates the composition gradient at that point, the curve approaching more nearly to the horizontal the greater the composition gradient. The figures need little discussion since they present the results better than can be done in words.

## THEORETICAL CONSIDERATIONS

As noted on an earlier page, concentrations in a mass undergoing diffusion may be calculated on the basis of Fick's law. In its application to the present case, and in the form most useful for



calculation of the concentration at any point in a diffusion cylinder, the equation<sup>1</sup> becomes

$$2c = c_0 \left[ \frac{2}{\sqrt{\pi}} \int_{\frac{-l-x}{2\sqrt{kt}}}^{\frac{l-x}{2\sqrt{kt}}} e^{-\beta^2} d\beta + \frac{2}{\sqrt{\pi}} \int_{\frac{-l-(2m-x)}{2\sqrt{kt}}}^{\frac{l-(2m-x)}{2\sqrt{kt}}} e^{-\beta^2} d\beta + \text{etc.} \right] I$$

where the term in brackets in the limits is successively  $x$ ,  $2m-x$ ,  $2m+x$ ,  $4m-x$ ,  $4m+x$ , etc., and where  $c$  is the volume concentration at any point at distance  $x$  from the base of the column,  $l$  is the thickness of the bottom layer of original uniform concentration  $c_0$ ,  $m$  is the total length of column,  $t$  is the time elapsed, and  $k$  the constant of diffusivity. For the examples in hand the series is rapidly convergent. With the aid of this equation we may, then, calculate the concentration at various points after a certain period of time and for a certain value of  $k$  (or, more simply, for a certain value of the product  $kt$ ) and draw a curve representing the theoretical distribution of concentration. Curves of this kind were drawn and it was found that in no case could a calculated curve be obtained that would coincide with the observed curve. Of the calculated curves a certain one was chosen and was plotted on each of the figures as a dotted curve. The theoretical curve chosen in each case was that which showed approximately the same concentration at the upper surface as that actually found. The curves therefore coincide at their upper ends, but at other depths wide divergence is shown between the full curve of actual concentration and the dotted curve of theoretical concentration. In all cases this divergence is of a systematic kind, the actual concentration showing a smaller gradient in the diopside-rich layers and a larger gradient in the diopside-poor layers than the theoretical concentration. This is shown particularly plainly in Figure 1, where the diopside-rich layers have reached practical uniformity while the upper layers show a very strong gradient. This uniform

<sup>1</sup> The equation is not so formidable as it appears,  $\frac{2}{\sqrt{\pi}} \int_0^q e^{-\beta^2} d\beta$  being merely the probability integral whose value, for various values of  $q$  in the limits, can be looked up in the tables.

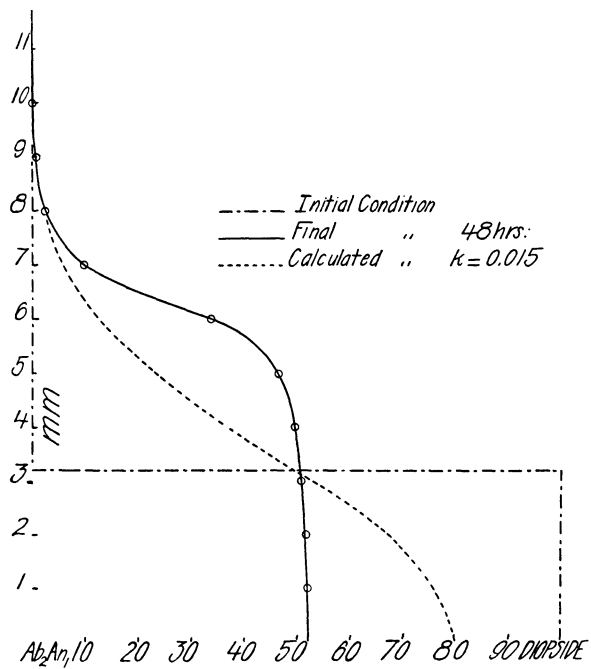


FIG. 1.—Diffusion experiment No. 27

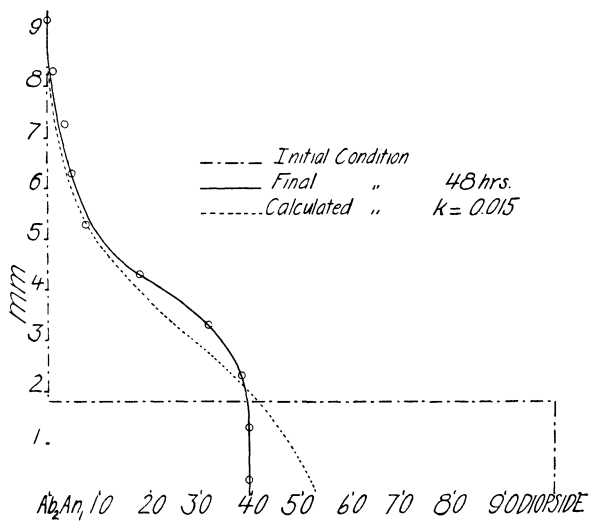


FIG. 2.—Diffusion experiment No. 24

divergence from theory may be explained by assuming that the coefficient of diffusivity is not a constant but is itself a function of concentration and is greater for diopside-rich mixtures than for those poor in diopside. In those experiments with aqueous solutions, where the highest degree of correspondence with theory is obtained, the solutions are always kept dilute so that the medium into which diffusion is taking place is sensibly constant. Under these conditions theoretical concentrations calculated on the basis of a constant value of the coefficient of diffusivity are in marked accord with observed values. In the present case, however, there is a continual and very important change in the nature of the diffusion medium as time progresses, and no constancy is to be expected in the value of the coefficient of diffusivity. There is no necessity, therefore, for regarding the results as showing divergence from Fick's law, the results being reconcilable with theory if it is assumed, as mentioned above, that the diffusivity is a function of concentration.

Einstein has developed for dilute solutions a theoretical relation between diffusivity and viscosity which makes them inversely proportional.<sup>1</sup> While experimental results do not entirely confirm his theory, they suggest its correctness if certain disturbing factors such as hydration could be evaluated.<sup>2</sup> At any rate, if we assume that the diffusivity is an inverse function of viscosity, we obtain a natural explanation of our experimental results. The viscosity of the diopside-rich mixtures is much less than that of the plagioclase-rich mixtures. The coefficient of diffusivity for the diopside-rich mixtures should be correspondingly greater, and this we have found to afford a natural explanation of the deviation from theoretical values calculated in the ordinary way. Moreover, as one would expect, this deviation is more marked for the plagioclase liquid  $\text{Ab}_2\text{An}_1$  whose viscosity is very much greater than that of diopside liquid, and less marked for the plagioclase liquid  $\text{Ab}_1\text{An}_2$  where the viscosity contrast is not so great, while liquid  $\text{Ab}_1\text{An}_1$  occupies an intermediate position in this particular (cf. Figs. 1, 3, and 5). Qualitatively, then, the experimental results suggest

<sup>1</sup> *Ann. d. Physik*, Vol. XVII (1905), p. 549.

<sup>2</sup> L. W. Öholm, *Medd. K. Vetenskapsakad. Nobelinstitut* 2, No. 26, p. 21.

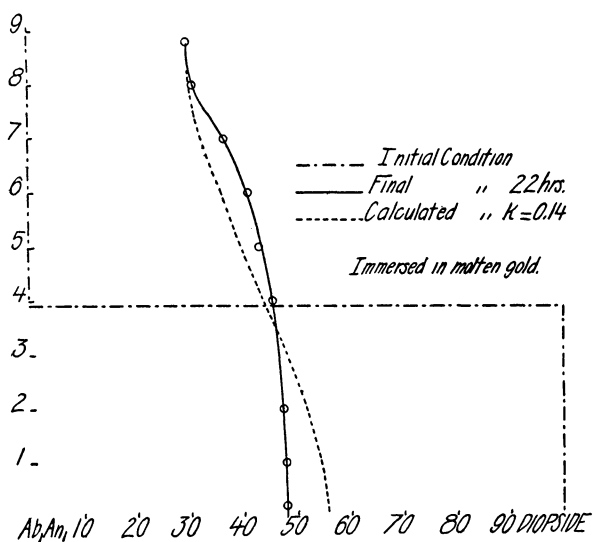


FIG. 3.—Diffusion experiment No. 21

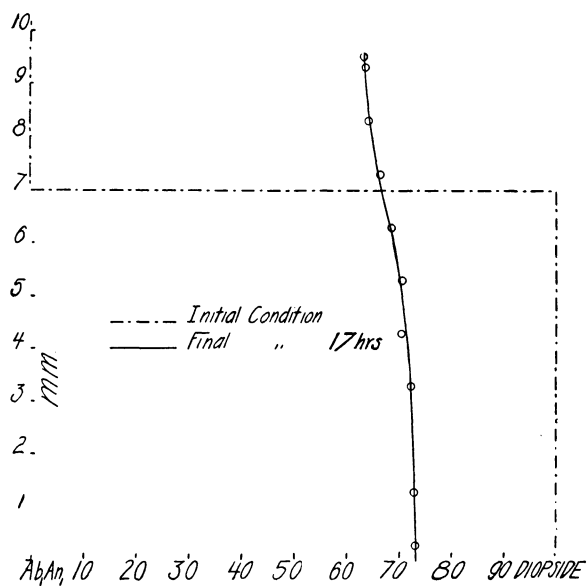


FIG. 4.—Diffusion experiment No. 37

agreement with theory if the variation of the coefficient of diffusivity is taken into account. It is possible, too, that from the observed values a definite quantitative relation between the coefficient of diffusivity and the concentration could be calculated, but the writer has not been able to find any attack upon a problem of this

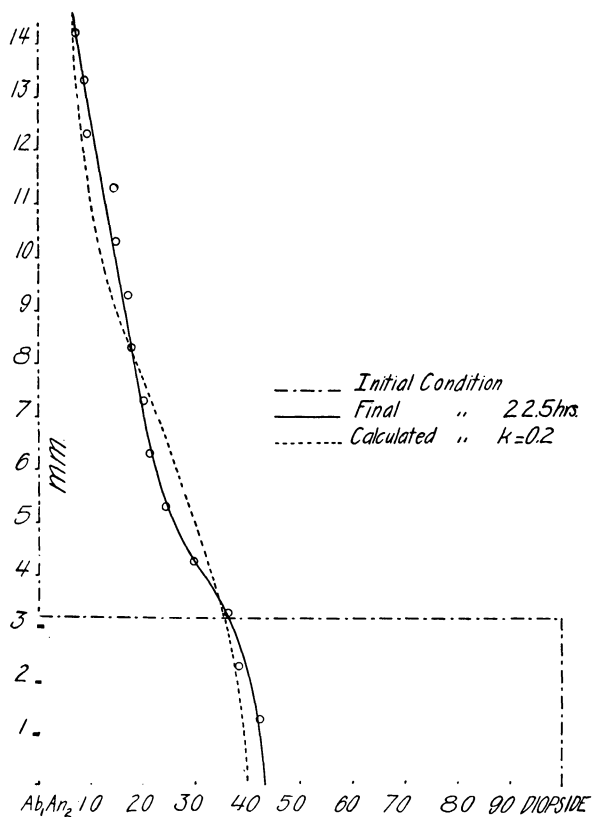


FIG. 5.—Diffusion experiment No. 25

kind in the various treatments of diffusion of concentration or of temperature. All of these adhere to a constant value of the coefficient of diffusivity. While in some respects it is highly desirable to check the present results more thoroughly along the lines indicated above, yet, for the purposes of the present paper, this is unnecessary. The results afford us very definite information as to the

magnitude of diffusion in silicate melts, which was the objective in mind when the work was undertaken.

#### VALUES OF DIFFUSIVITY

We cannot speak of a diffusivity "constant" in connection with the present results, but we may take the amount of diopside which penetrates to the surface layer as an indication of the average diffusivity of diopside in a liquid mixture of diopside and plagioclase. In this sense we find the "average diffusivity" of diopside in  $\text{Ab}_2\text{An}_1$  mixture from Experiment No. 24 (Fig. 1),  $k=0.015$  in  $\text{cm}^2$  per day, in  $\text{Ab}_1\text{An}_1$  mixture from Experiment No. 21 (Fig. 3),  $k=0.14$ , and in  $\text{Ab}_1\text{An}_2$  mixture from Experiment No. 25 (Fig. 5),  $k=0.2$ . We therefore observe a progressive increase in the value of  $k$  with increase in the amount of anorthite in the diffusion mixture. Since it is well known that plagioclases rich in anorthite afford less viscous liquids than those rich in albite, we have further evidence of the increase of rate of diffusion with decrease of viscosity. If we compare the results of Experiment No. 21 (Fig. 3) and 37 (Fig. 4), we find again an increase in the value of the diffusivity, being  $k=0.14$ , and  $k=0.3$ , respectively.<sup>1</sup> In both these examples, however, the plagioclase  $\text{Ab}_1\text{An}_1$  was used, the difference being that an increasing proportion of diopside was added. As a consequence, a higher value of the diffusivity is found for the mixture which was richer in diopside and therefore of lower viscosity. All of the results are therefore consistent with the assumption that the diffusivity varies inversely with the viscosity, which is in turn dependent on composition.

By way of comparison of the diffusivities here found with measured values of diffusivities for other substances, it may be noted that for common salt diffusing in water  $k=1$  at  $15^\circ\text{C}$ ., for gold in molten lead at  $492^\circ\text{C}$ .,  $k=3$ , for solid gold in solid lead at  $150^\circ\text{C}$ .,  $k=0.0043$  in the same units as those used above. The

<sup>1</sup> In Figure 4 no calculated curve is shown for the reason that the calculated curve for  $k=0.3$  sensibly coincides with the observed curve. Since the final result will be uniformity in all cases, whether the diffusivity varies with composition or not, a close approach of the calculated curve to the observed curve is to be expected in cases where diffusion is far advanced (Fig. 4). On the other hand, where the upper layers have not yet been affected, the greatest divergence between observed and calculated values is to be expected (Figs. 1 and 2).

diffusivities obtained for the silicates are, therefore, much smaller than those of salts in solution and those of molten metals, but much greater than those of solid metals. Some of the higher values obtained for the silicates are comparable with those of certain relatively viscous organic liquids. The diffusivity constant of glycerine in propyl alcohol at 17°C. is, for example, approximately 0.2.

#### APPLICATION OF RESULTS

It is not at all likely that the diffusivities of substances in mutual solution in rock magmas can be significantly greater than those determined for the plagioclase-diopside mixtures, and in many viscous magmas they would no doubt be considerably less. For the purpose of applying the results to diffusion problems in petrogenesis a value has been taken very close to the highest, viz., 0.25, which is at the same time convenient in calculations. The Soret action is one of the diffusion phenomena that has been considered of possible importance in magmas. It has been found in the laboratory that if a tube containing a solution is heated at one end and cooled at the other there is usually a concentration of the solute toward the cold end which depends upon the difference of temperature, the relative concentrations being, for many cases, inversely as the absolute temperatures. In cooling magmas the margin must be regarded as having a lower temperature than the interior, and there should presumably be a tendency toward a greater concentration of some substance or substances at the cooler margin. This introduces the possibility of composition differences in different parts of an entirely liquid magma, the differences being brought about by diffusion. If cooled entirely by conduction, the temperature of a magma brought into contact with cold country rock should at the border quickly assume a value midway between that of the magma and that of the country rock. For a long period thereafter cooling at the margin is very slow (see Fig. 6).<sup>1</sup> We may imagine that the original temperatures of the magma and that of the surrounding rocks are such that during this long period of maintenance midway between them the magma is still above its temperature of beginning of crystallization. Here we would have

<sup>1</sup> See also Lane, *Ann. Rept. Geol. Surv. Michigan for 1909*, Fig. 18, p. 152.

the most favorable case conceivable for the establishment of a composition gradient as a result of a temperature gradient according to the Soret principle. These conditions would evidently obtain either when the temperature of the magma was very much above the crystallization temperature, or when that of the surrounding rock was not very much below it, the latter being the more likely case. The magma intruded into hot surroundings, perhaps into a cognate intrusive not yet cooled, is, therefore, the most favorable

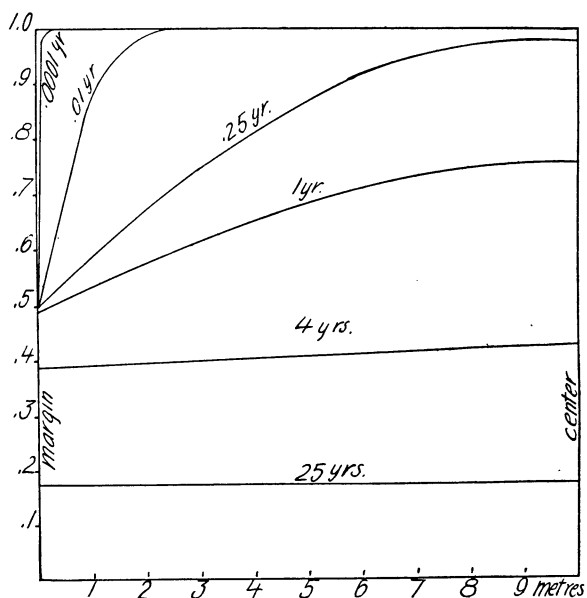


FIG. 6.—Curves of cooling of an intrusive igneous sheet 20 m. thick

subject for the working of the Soret action. Yet when we realize that the diffusivity of mass is, according to our determinations, from 10,000 to 100,000 times smaller than the diffusivity of temperature in rocks, it is apparent that the temperature of any igneous body will fall too rapidly to allow sufficient time for the Soret phenomenon to manifest itself.

This statement may perhaps be more readily appreciated if the Soret action is stated more definitely as a diffusion problem. In order to do so we may assume that the osmotic pressure is



proportional to the absolute temperature and that for this reason diffusion takes place until the concentration is inversely proportional to the absolute temperature. In other words, the effective concentration is, initially, inversely proportional to the absolute temperature, and diffusion takes place until the effective concentration is uniform. In applying these considerations to a cooling mass of rock, we may take for simplicity a tabular body. A solution of the problem of the cooling of such a body is given by the equation

$$\theta = \frac{\theta_0}{\sqrt{\pi}} \int_{\frac{-l-x}{2\sqrt{kt}}}^{\frac{l-x}{2\sqrt{kt}}} e^{-\beta^2} d\beta$$

where  $\theta$  is the temperature at any point distant  $x$  from the margin,  $\theta_0$  the original temperature of the magma, the temperature of the wall rock being taken as zero and  $l$  is thickness of the intrusive.

If we take a tabular body of thickness 20 m. (i.e., 10 m. from center to margin) we may calculate the temperature in any plane at given distance from the margin at the end of any period of time. The results of such calculations are shown graphically in Figure 6, the curves representing the distribution of temperature at the end of various periods of time if the diffusivity is taken as 0.0118 in cm.<sup>2</sup> per second. In this figure the temperature scale has no necessary absolute significance, 0 of the scale being merely the initial temperature of the surrounding rock and 1 of the scale being the initial temperature of the magma. It will be noted that at the end of one year the temperature at the margin is about halfway between the initial temperature of the surrounding rocks and that of the magma, while the temperature at the center is much higher. If it is supposed that the whole mass is still above its crystallization temperature, then the Soret action should be operative, that is, the effective concentration at any point should be proportional to the absolute temperature, and diffusion should take place until the effective concentration was uniform. Partly for simplicity and partly for the sake of obtaining an especially marked Soret effect we shall assume that the temperature scale of Figure 6 represents

absolute temperature, i.e., 0 of the scale is 0° absolute and 1 of the scale is 1000° absolute. After one year the temperatures at the margin and at the center are 490° and 760° respectively. Then the effective concentration at the center should be  $\frac{76}{49}$  times that at the margin and diffusion should take place until the effective concentration is uniform, or until the real concentration at the center is  $\frac{49}{76}$  times that at the margin. The problem is to find how long a time it would require for this diffusion to take place. Infinite time would, of course, be required to allow the process to go to completion, but we may find the time needed to give any assigned approach to this condition.

As a first step we may calculate the time necessary for the acquirement, from any arbitrary initial condition, of a concentration gradient represented by the curve showing the thermal gradient at the end of one year. This may be done by assuming a condition analogous to our experiments, viz., that all the material was first concentrated in a meter layer and by diffusion had acquired the gradient referred to. With the aid of equation (I) we find this to be very nearly true when  $\sqrt{kt}$  in the limits of the integral has the value 500. If we take  $k$  as having a value close to the highest found in any of the experimental determinations, viz., 0.25, then  $t = 10^6$  days. But this is not the time we wish to know; it is that required to go on from this condition to practical uniformity. Again we find from the equation that practical uniformity (1:0.996) is obtained from the arbitrary initial condition when  $\sqrt{kt} = 1000$  or when  $t_1 = 4 \times 10^6$  days. From this we get the desired time  $t_1 - t = 3 \times 10^6$  days, or nearly 10,000 years. This shows that it would need about 10,000 years to obtain nearly the full theoretical Soret effect required by the curve of temperature distribution after one year in a mass of the dimensions chosen. In the meantime, as shown by the curves of Figure 6, the whole mass would have cooled to the temperature of the surrounding rocks. Even if we imagine it to be still above its crystallization temperature at the end of four years, it will be noted that most of the temperature gradient has been destroyed at that time so that

there is no reason for the action continuing even for four years. It should be observed that, although the times have been computed for a body of a definite size, the solution is really of a general nature, for if the body were  $n$  times as thick, the time on the one-year curve would be changed to  $n^2$  years and the time required for the Soret phenomenon would be  $n^2$  times as large. Nothing is gained, therefore, for the Soret effect by making the body larger or smaller.

In assuming that the scale of Figure 6 represents absolute temperature, we have, of course, taken an impossible condition for any body of rock. This would mean that the surrounding rocks were initially at  $0^\circ$  absolute and the magma had not yet begun to crystallize at  $490^\circ$  absolute =  $217^\circ\text{C}$ . The assumption was made on account of the convenience of referring both concentration and temperature gradients to the same curve, but even if we make reasonable assumptions as to the temperature of the magma and of wall rock, our conclusion will not be affected. We may even assume that the Soret effect for silicates is many times that deduced from the theoretical (absolute temperature) relation, yet the outstanding fact remains that the time required to produce a significant amount of concentration of material by diffusion is enormously greater than that required for the mass to cool off.

It may be noted that in speaking of a concentration toward the cool margin no mention has been made of what is concentrated. The reason is, of course, that it is not known. Ordinarily it is stated that the solute is concentrated toward the margin, but no distinction of solvent and solute can be applied to magmas. In conclusion, then, it may be stated that no concentration of any substance toward the cool margin could occur in appreciable amount in the time available for such action in a cooling mass of completely molten rock.

#### DIFFUSION TOWARD MARGIN DURING CRYSTALLIZATION

There is, however, another case of diffusion of material toward the cool boundary for which we know the nature of the material that should move in that direction. Harker lays stress on the fact that in any cooling mass of magma there should be a time

when crystallization of an early-formed mineral *A* takes place only near the border, the rest of the mass being still above the temperature of crystallization. The greater concentration of the substance *A* in the interior of the mass where none has yet precipitated should constitute a driving force tending to cause that material to diffuse toward the margin. This case may be stated fairly simply as a definite diffusion problem. When the temperature of a thin layer at the margin has fallen to such a value that a certain fraction of the amount of substance *A* in that thin layer has precipitated, then the magma in this layer is saturated with *A*. If this condition is maintained for an infinite period of time, the whole body of magma will eventually acquire the same concentration in *A* as this marginal saturated solution<sup>1</sup> and all of substance *A* in excess of this concentration will be precipitated at the margin. If we assume the contact surface plane as in a tabular mass, this is essentially the same problem as the heat-conduction problem involved in the cooling of a sheet of metal one face of which is kept at constant temperature. A solution of the problem is given by the equation:

$$c = \frac{2c_0}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta$$

which gives the concentration *c* in terms of the original concentration *c*<sub>0</sub> at any point at distance *x* from the margin after the time *t*, the concentration of the marginal saturated solution being taken = 0.

Values of *c* for various values of *x* and *t* have been calculated for a diffusivity 0.25 in cm.<sup>2</sup> per day, approximately the highest experimental value, and are plotted as concentration curves in Figure 7. The figure shows that after two-thirds of a year the precipitating effect has been felt for a distance of 0.33 m. from the margin, all the rest of the magma being entirely unaffected. After sixty-four years the precipitating effect has been felt for a

<sup>1</sup> Neglecting the Soret effect.

distance of 3.3 m. while all the rest of the magma is unaffected, and similarly for the other concentration curves.

We can, moreover, determine from the figure the amount of material that would be precipitated at the margin at the end of any period of time. At the end of infinite time the concentration curve would correspond with the axis of abscissae, that is, the concentration at all points is zero of the scale, or equal to the concentration of marginal saturated solution. The whole area

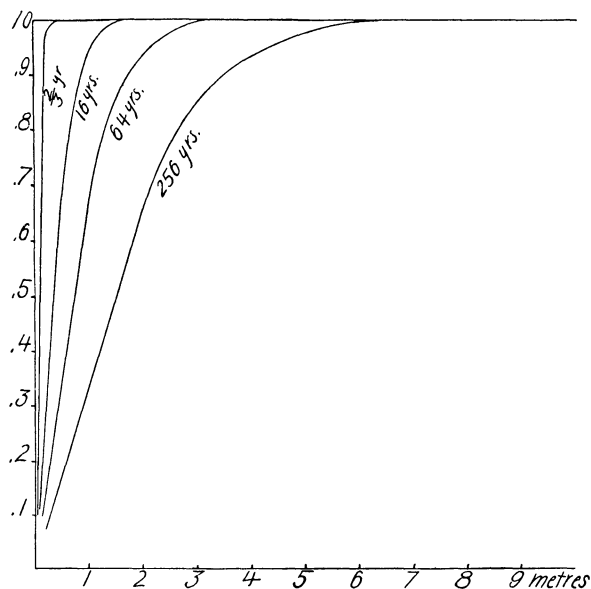


FIG. 7.—Curves of concentration in an igneous mass showing diffusion of material toward a cool boundary.

of the rectangle between the extreme ordinates of the figure represents, therefore, on a certain arbitrary scale the amount of material which would be removed in bringing the whole magma to the concentration of the marginal saturated solution. On the same scale the area lying above and to the left of the concentration curve for any time represents the amount of material removed during that time. We may take a specific case and imagine that the mineral precipitated at the margin is, say, amphibole, which occurs in the magma to the extent of 20 per cent, and that the

cooling of the marginal layer had proceeded until one-fourth of the amphibole contained in that layer (or 5 per cent of the layer) had been precipitated. If this condition were maintained the precipitation of amphibole at the margin would proceed by diffusion from the parts not yet cooled below the temperature of precipitation of amphibole. At the end of two-thirds of a year a proportion of the excess amphibole would be precipitated equal to the area between the one-year curve and the axis of ordinates. Regarding this area as a triangle of base sensibly 0.3 m. and assigning any arbitrary total thickness  $x$  to the mass, then the thickness of the amphibole deposit in meters would be

$$\frac{0.3}{2} \cdot \frac{1}{x} \cdot \frac{5}{100} x.$$

That is, a deposit 0.0075 m. or  $\frac{3}{4}$  cm. thick would be formed on the margin in two-thirds of a year. Its thickness is independent of the total thickness of the mass of magma and all of it would be derived from a layer of magma 33 cm. thick. After sixteen years the deposit would be about 2 cm. thick, all coming from a layer of magma about 1.5 m. wide. After two hundred and fifty-six years the deposit would be about 8 cm. thick, all from a border portion less than 7 m. wide.

It is apparent that the possible results of diffusion after the manner postulated are exceedingly small. A mass of magma large enough to remain in the necessary condition for two hundred and fifty-six years would have a border phase 8 cm. thick. By necessary condition is meant that the margin should be cooled within its crystallization range and the main portion of the mass be not yet so cooled. The indications are that the mass would require to be at least 300 m. thick and be intruded under special conditions of temperature of magma and of wall rock, and the border phase would then be insignificant. Even by making more liberal assumptions as to the amount of chilling at the margin, say, a chilling sufficient to precipitate 25 per cent of the magma solution, the possible border phase would be increased in magnitude only five times. Moreover, as one increases the extent of marginal chilling, a stage is soon reached where so much precipitation takes

place in the marginal phase that no diffusion into that region can occur. One then arrives at a method of formation of a border phase that has been suggested by Daly, who regards the border phase as a chilled phase having the composition of the original magma.<sup>1</sup>

#### FORMATION OF REACTION RIMS

We have seen in the foregoing that the movement of large quantities of material through long distances by diffusion in a magma cannot be credited when the relatively rapid rate at which the magma must cool is considered. On the other hand, diffusion through short distances is to be expected, and such phenomena as the formation of reaction rims about foreign inclusions are readily to be attributed to diffusion. At the same time it should be noted that a rather wide reaction border will require a very considerable period of time for its formation if diffusion alone is active. Figure 7 enables one to form an idea of the period of time required for the diffusion of material from an inclusion to various distances in the surrounding medium if the scale of concentrations is reversed, that is, if zero is placed at the top and one at the bottom. The solution is by no means a rigid one for a small inclusion, but for a large slablike inclusion is sufficiently good to enable one to draw general conclusions. The figure shows that after sixty-four years the effect of the inclusion is barely felt for about 3 m. and is strongly felt (one-half saturation) for not more than 1 m. These considerations suggest that the formation of reaction rims up to 2 m. thick, such as those described by Ussing, about inclusions of quartzite in augite syenite at Kangerdluarsuk would require a period of time of the order of magnitude of one hundred years if diffusion alone were operative.<sup>2</sup>

The growth of crystals is itself largely dependent upon diffusion, but no quantitative estimate of the rate of growth is possible without some knowledge of the concentration gradient along which flow of material takes place, that is of the degree of supersaturation possible in the liquid interstitial to the crystals. The

<sup>1</sup> *Igneous Rocks and Their Origin*, p. 237.

<sup>2</sup> *Geology of the Country about Julianehaab, Greenland*, p. 362.

fact that rocks are normally millimeter-grained rather than centimeter- or meter-grained even in large masses is, however, a tribute to the slowness of diffusion in magmas. The fact that certain conclusions are reached above on the assumption that diffusion acts alone should not be taken as indicating that the writer believes that no other processes could occur. To account for the extremely coarse grain of many pegmatites, for example, it seems necessary to assume circulation of solutions, and in many other cases cited circulation (convection) would be inevitable.

#### SUMMARY

The rate of diffusion in certain silicate melts has been determined experimentally by permitting diffusion against gravity of a heavy liquid into a lighter liquid. The concentration curves found are not coincident with any theoretical curves calculated on the basis of a constant value of the diffusivity, but can be interpreted on the assumption that the diffusivity varies with concentration and is less for concentrations corresponding to more viscous liquids than for those corresponding to less viscous liquids. Taking as representative of the "average diffusivity" the amount of material which penetrates into the upper layer, the following values of the average diffusivity ( $k$ ) were found: for diopside into  $\text{Ab}_2\text{An}_1$ ,  $k=0.015$ ; for diopside into  $\text{Ab}_1\text{An}_1$ ,  $k=0.14$  to  $0.3$ , depending on the proportions; and for diopside into  $\text{Ab}_1\text{An}_2$ ,  $k=0.2$ , all in  $\text{cm}^2$  per day.

The value  $0.25$  (close to the maximum experimental value) is taken as probably representing a fair estimate of diffusivity in magmas, and with this as a basis it is shown that such phenomena as the formation of border phases about large bodies of igneous rock by diffusion cannot be considered possible in the time available for such action in a cooling magma. On the other hand, the formation of reaction rims about inclusions may be attributed to diffusion, though for very wide rims a considerable period of time will be required.